

REMARKS

I. STATUS OF THE CLAIMS:

Claims 1-8 are pending. Claims 1 and 2 have been amended and claim 9 has been canceled. Support for the amendment to claim 1 can be found in the original application as filed at page 4, lines 17 to 27. Applicants respectfully submit that no new matter has been added by virtue of this Amendment.

II. REJECTION UNDER 35 U.S.C. § 102(b)

A. Rejection in view of U.S. Patent No. 5,183,545 to Branca et al.

In the Office Action, the Examiner rejected claims 1-4 and claims 6-8 on the grounds of being anticipated by U.S. Patent No. 5,183,545 ('the '545 patent') to Branca et al. The Examiner stated that "[t]he Branca et al. patent sets forth a multilayer composite membrane having at least two layers of distinctly different porosity where the greater porosity is against the anode and the lesser porosity is against the cathode...The invention further discloses the thickness of the membrane and Gurley air flow and the methanol bubble point, all of which indicate that the pore diameter and layer thickness of the diaphragm are in the same range as the applicants instant invention, absent evidence to the contrary."

This rejection is respectfully traversed. Amended independent claim 1 of the present invention recites:

1. A permeable membrane diaphragm of different layers for electrolytic cell, comprising:

a flow-controlling permeable layer, which comprises a thin liquid permeable micro-porous membrane or several thinner similar membranes made of fluoro-containing polymers; wherein the flow-controlling permeable layer is mounted toward the anode;

a diffusion-restricting permeable layer, which comprises a thick permeable perforate film, sheet or cloth, or several thinner similar films, sheets or cloths made of anti-corrosive materials which are different from those of the flow-controlling permeable layer; wherein the mean pore diameter of the diffusion-restricting permeable layer is at least 5 times larger than that of the flow-controlling permeable layer, and the thickness of the diffusion-restricting permeable layer is at least 1 times larger than that of the flow-controlling permeable layer; wherein the diffusion-restricting permeable layer is mounted toward the cathode;

optionally a protective layer, which comprises one or more liquid permeable film, sheet or cloth made of anti-corrosive materials; wherein the protective layer covers the micro-porous membrane of the flow-controlling permeable layer to protect it; and

optionally a fluid impermeable frame made of anti-corrosive material;
wherein the fluid impermeable frame is around the above-said layers.

As pointed out by the Examiner, Branca et al. disclose a composite, porous, liquid permeable diaphragm of a multilayer structure of discrete bonded layers of porous, expanded polytetrafluoroethylene (ePTFE). Thus, each layer of the multilayer diaphragm of Branca et al. is made of expanded polytetrafluoroethylene (ePTFE), which is a microporous membrane. However, as recited in claim 1 of the present invention, the permeable membrane diaphragm comprises at least two different layers, one of them being a microporous membrane made of a fluoro-containing polymer and the other being a perforated film, sheet or cloth, which is not a microporous membrane, made of anti-corrosive materials different from the material of the microporous membrane. Therefore, the structure of the diaphragm as recited in independent claim 1 of the present invention is different from that described by Branca et al.

Moreover, as stated by the Examiner, Branca et al. defines the asymmetric structure of their diaphragm with specific gravity. Applicants submit that it is well known for a person skilled in the art that specific gravity of a permeable membrane is determined by the density of the material from which the membrane is made and the porosity of the membrane. Applicants further submit that porosity of a permeable membrane is obtained from the total volume of the pores contained in the permeable membrane divided by the total volume of the permeable membrane, and it is a function of the mean pore diameter, the mean pore length and the amount of the pores. Therefore, specific gravity can be used to define the asymmetric structure of the two membranes only when two membranes are made of same material and the difference between their mean pore diameters is not more than 1 times that of the smaller mean pore diameter. Therefore, Branca et al. uses specific gravity to define the asymmetric structure of their permeable membrane diaphragm because the multiple layers are made of the same material, i.e., expanded polytetrafluoroethylene. Otherwise, the difference of specific gravity shall not be used as a parameter to define the asymmetric structure of the membranes.

The asymmetric structure of the permeable membrane diaphragm of the present invention relates to the different materials used for the flow-controlling layer and the diffusion-restricting layer, the different pore sizes of the two layers (one being a microporous membrane and the other not being a microporous membrane with a mean pore diameter of the diffusion-restricting layer at least 5 times larger than that of the flow-controlling layer), as well as, the different thicknesses of the two layers (the thickness of the diffusion-restricting layer being at least 1 times larger than that of the flow-controlling permeable layer). However, the specific gravities of the two layers of the present invention may be different, close or identical given that different materials may be used for the flow-controlling layer and the diffusion-restricting layer. Therefore, the difference of specific gravities defined by Branca et al. does not teach or suggest asymmetric structure of the permeable membrane diaphragm of the present invention.

In addition, as mentioned by the Examiner, Branca et al. describes a multilayer composite membrane having at least two layers of different pore size, wherein the larger

pore size faces the anode and the smaller pore size faces the cathode. However, such arrangement is opposite of the approach of the present invention. In the permeable membrane diaphragm of the present invention, the permeable layer with smaller mean pore diameter is mounted toward the anode and the permeable layer with larger mean pore diameter is mounted toward the cathode. Therefore, Branca et al. does not teach or suggest the same arrangement of the permeable membranes in the diaphragm as claimed in present claim 1. Therefore, Branca et al. does not anticipate claim 1 of the present invention, nor does this reference anticipate claims 2-8 which are dependent on claim 1.

Furthermore, Branca et al. describes that there are at least two microporous membranes in the multilayer structure, which are made of the expensive material, ePTFE. In the present invention, it is possible to use only one microporous membrane, therefore the production cost of the diaphragm of the present invention can be reduced.

In addition, the Examiner mentioned that the methanol bubble point 0.7 psi to 40 psi disclosed by Branca et al indicates that the pore diameter of the diaphragm is in the same range as the present application. Applicants point out that in dependent claim 6 of the present application the mean pore diameter of the diffusion-restricting layer is in the range of 5-50 μ m and in dependent claim 7 of the present application the mean pore diameter of the diffusion-restricting layer is in the range of 10-20 μ m. A person skilled in the art will readily know that by using the same method ASTM F 316-80 as used by Branca et al. for measuring the methanol bubble point, the methanol bubble point of the diffusion-restricting layer of the present invention will certainly be much lower than 0.7 psi, which indicates a much larger mean pore diameter. Therefore, the diaphragm containing the diffusion-restricting layer of the present invention is significantly different from the diaphragm containing only microporous membranes as described by Branca et al.

Therefore, Applicant respectfully submits that the '545 patent reference does not anticipate claim 1 of the present invention, nor does this reference anticipate claims 2-9

which are dependent on claim 1. Thus, Applicants respectfully request that the Examiner remove the anticipation rejection of claims 1-4, 6-8 over the '545 reference.

REJECTION UNDER 35 U.S.C. § 103(a)

A. Rejection in view of U.S. Patent No. 5,183,545 to Branca, et al. in combination with U.S. Patent No. 4,921,587 to Dong.

In the Office Action, the Examiner rejected Claim 5 under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent No. 5,183,545 to Branca in combination with U.S. Patent No. 4,921,587 to Dong. Specifically, the Examiner stated that "[t]he subject matter as a whole would have been obvious to one having ordinary skill in the art at the time the instant invention was made because even though the prior art of Branca et al does not disclose that propylene maybe used in the making of a multilayer diaphragm, the prior art of Dong et al shows that it is known to the person having ordinary skill in the art to use such a material in combination with PTFE or in place of PTFE."

This rejection is respectfully traversed. Amended independent Claim 1 of the present invention is as presented above. Claim 5 of the present invention is dependent on Claim 1 and recites:

5. The permeable membrane diaphragm of different layers for electrolytic cell of claim 1, wherein the matrix of the diffusion-restricting permeable layer is polypropylene.

Applicants respectfully submit that Branca et al. does not teach or suggest a permeable film diaphragm comprising a microporous membrane as the flow-controlling permeable layer and a perforated membrane (which is not a microporous membrane) made of a material different from that of the microporous membrane as the diffusion-restricting layer as recited in independent claim 1 of the present invention.

Applicants submit that Dong et al. describes a permeable porous diaphragm composed of an assembly having a plurality of layers of a microporous polyolefin film or a composite material comprising a supporting fabric resistant to degradation upon exposure to electrolyte and the microporous polyolefin film, wherein the supporting fabrics include fabrics composed of polyethylene, polypropylene, polytetrafluoroethylene, fluorinated ethylenepropylene, polychlorotrifluoroethylene, polyvinyl fluoride, polyvinylidene fluoride and mixtures thereof. However, the polyolefin supporting fabric disclosed by Dong et al. is not a diffusion-restricting layer as disclosed in claim 5 of the present application. In the Dong patent, the supporting fabric is not always needed for the diaphragm, and its material, structure and function all correspond to those of the optional protective layer as recited in claim 1 of the present application. Meanwhile, in the presently disclosed invention, the diffusion-restricting layer is an essential part of the diaphragm and it has specific mean pore diameter and thickness as compared with the flow-controlling layer. Dong et al. do not define the mean pore diameter of the supporting fabrics. Moreover, Dong et al. do not define which electrode the microporous polyolefin film is facing and which electrode the supporting fabric is facing.

Claim 5 of the present application depends on claim 1 and it claims a permeable membrane diaphragm comprising a flow-controlling permeable layer, which is a microporous membrane made of fluoro-containing polymer and facing the anode; and a diffusion-restricting permeable layer, which is a perforated film made of polypropylene and facing the cathode. As disclosed in lines 2-11 on page 4 of the present application, the present invention provides a permeable membrane diaphragm of an asymmetric structure formed by different layers, wherein the thin layer with very small pore size is mounted toward the anode and this layer has low electric resistance and high flow resistance and can prevent insoluble particles from entering into the layer; and the thick layer with larger pore size is mounted toward the cathode, so it can discharge the deposition of hydroxide easily without sacrifice its capability of restricting the diffusion of OH⁻ groups from the cathodic compartment to the anodic compartment.

In support of the patentability of the present invention, Applicants attach herewith an unpublished technical report that is an in-house article about the technology relevant to the present application.

Accordingly claim 5, which is dependent on claim 1, is not obvious over the Branca et al. patent in combination with the Dong patent. Therefore, Applicants respectfully request that the Examiner's obviousness rejection as to claim 5 be removed.

III. REJECTION UNDER 35 U.S.C. § 112

In the Office Action, the Examiner rejected claim 9 under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

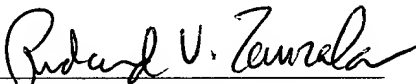
As claim 9 has been cancelled, Applicants respectfully request that the rejection be removed.

VI. CONCLUSION

This Response is being submitted together with a petition for a one-month extension of time under 37 C.F.R. § 1.136(a) from December 11, 2006 to January 11, 2007. A check in the amount of \$60.00 is enclosed herewith to cover the fee due under 37 C.F.R. § 1.17 (a)(1) for a small entity. It is believed that no other fees are due. If, however, it is determined that any additional fees are due or that any fee has been overpaid, the Commissioner for Patents is hereby authorized to charge said fee or credit any overpayment to Deposit Account No. 50-0552.

Respectfully submitted,

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STUDY ON THE STRUCTURAL STABILITY OF NON-ASBESTOS DIAPHRAGM

I. Introduction

Since the 1930s, the deposition-asbestos diaphragm has been applied widely in chlor-alkali plants as an important part of a diaphragm cell. The diaphragm cell is a key equipment of the diaphragm process. This is a unique process for its ability of directly using natural bittern to produce chlorine and caustic soda. Because bittern is much cheaper than salt, the diaphragm process is cost-effective. Many plants have been built where bittern resources are abundant. It has been believed that diaphragm process is more suitable than other process including the ion-exchange membrane process. However, the asbestos diaphragm has many disadvantages such as asbestos pollution, short lifetime and inability to handle high operational current fluctuations. The invention of DSA technique prompted the research on the non-asbestos diaphragms since the 1970s. But these studies failed to find a functional non-asbestos diaphragm.

Prior to non-asbestos diaphragms, which are designed to have the same structure as the deposition asbestos diaphragm does, a prevailing theory on the structure of diaphragm is believed. Following this theory, the structure of a deposition asbestos diaphragm is stable during its operation circle and only its chemical components are changing. In the end of the operation life, a lot of chemical components are changed and the structure therefore is destroyed. However, a laboratory test will prove that this theory is wrong. In a laboratory cell, a deposition asbestos diaphragm was assembled and brine was fed, but no direct current was applied. After a few hours, the diaphragm was swollen to form a loose layer and the brine passed through the diaphragm at increased velocity under a steady hydraulic pressure difference; later on, a direct current was applied through the cell and the diaphragm changed to form a tight layer and the brine convectional flow reduced to a steady velocity under a steady hydraulic pressure difference. From the test, we believe that the fibers of the diaphragm are separated by the Brownian movement brine molecules and are pressed together by the electric osmosis and electrophoresis when a direct current is applied. The deposition asbestos diaphragm is therefore not stable in structure and is hard to simulate; in addition, some disadvantages of this diaphragm were correlated with its unstable structure.

A stable structure of a non-asbestos diaphragm may make it easily overcome the



disadvantages of the deposition asbestos diaphragm and leads to exploration on feasible processes and materials to manufacture such kind of useful non-asbestos diaphragms. A critical issue for this stably structured non-asbestos diaphragm is its ability to meet customer requirements of chlor-alkali plants. These requirements may include: (1) even application of the direct current throughout the diaphragm; (2) low electric resistance; (3) being non-electrode; (4) allowance of solution pass through but separation of gases formation and evolution on anodes and cathodes respectively; (5) higher current efficiency of the diaphragm cell; (6) adequate electrolyte concentration in the cell; (7) easy, safe and pollution free operation; and (8) low investments and high profits. These requirements are based on electricity cost, electrochemical principles, hydraulic and other engineering requirements and economic evaluation, though some of them are contrary with each other. In order better to evaluate these requirements, it is therefore necessary to build a mathematic model to elucidate the relationship between the structure and performance of diaphragms. The model would be built upon scientific principles and validated through laboratory tests. Results would be used to search for a good non-asbestos diaphragm.

II. Functions of a micro-porous Layer

A stably structured non-asbestos diaphragm should be an insulator because it contacts the cathode of the cell. There are many passages through the insulator and the solution may pass through the insulator while passages are small enough to be able to separate bubbles. Because the direct current is conducted by the solution in passages, passages should be distributed over the insulator evenly.

Suppose a direct current is applied through the diaphragm of a cell, the intensity of the current is I , the potential drop is V at the applied current, and the resistance of the diaphragm is R . The diaphragm has an area of A with a thickness of T . Passages of the diaphragm have a total area of F and a mean length of L . The ratio of F to A and ratio of L to T are α and β , respectively. Passages are filled with a sodium chloride solution with a specific resistance of R_0 . According to Ohm's law,

$$V=IR \quad (1-1)$$

$$R= R_0\beta T/\alpha A= R_0 L/F \quad (1-2)$$

When the current is conducted through the sodium chloride solution, NaOH is formed on the cathode of the cell. According to the Faraday's law, the amount of NaOH is $I \cdot q \cdot t$ during the time length of t . Here, q is the Faraday's constant of NaOH. During

the same time t , the solution passes through the diaphragm's passages at a mean velocity of w . When the cell is operated under a steady condition, the volume of electrolyte flowing out of the cell nearly equals to the volume, of solution passed through the diaphragm during the same time t . Therefore, the volume of the electrolyte is F^*w^*t and the concentration of NaOH of the electrolyte C becomes,

$$C = I^* q^* t / (F^* w^* t) = I^* q / (F^* w) \quad (2-1)$$

The solution passes through the diaphragm of cell causes a pressure drop Δp , and in operation this required pressure drop is maintained by a liquid level difference between the anode and cathode compartments of the cell. Under normal operation conditions, w is very small, so the flow of solution follows Poiseuille's formula as it passes through passages of the diaphragm, then

$$\Delta p = 32\mu wL/D^2 \quad (2-2)$$

Here μ is the viscosity of the solution. D is the mean diameter of passages. W and L are the same as said above. Because Δp is formed by a difference of levels of the solution $\Delta p = \rho gH$, here p is the density of solution, g is the acceleration of gravity and H is the difference of levels.

From equations of (2-1), (1-2) and (1-1), let these values to substitute Δp , w , L in the equation (2-2) to get

$$\rho gHD^2 = 32\mu qIP/R_0C \quad (2-2a)$$

Because p , g , μ , q and R_0 are constants at a definite condition, we may get a constants group $K = \rho gR_0/32 \mu q$ and substitute to (2-2a). Then,

$$KHD^2 = IR/C = V/C \quad (2-3)$$

Equation (2-3) may be proved by a laboratory experiment as follows:

A laboratory cell is comprised of an anode compartment that is made from titanium and a cathode compartment that is made from steel. The area of its electrodes is 50cm^2 . Some micro-porous membranes, which was made by using a process of a patent CNZL94112057.0, and whose mean diameter of pores were measured by using a process of ASTM F316-86, are covered on the cathode of the cell as a diaphragm.

Membranes have the same mean diameter of-pores for each experiment, and different diameters and different amounts of the membrane are tried in different experiments. Before each experiment, membranes are covered on a PTFE plate on which a square hole is opened. The plate is then inserted vertically into a beaker. The beaker is filled with a sodium chloride solution containing NaCl 300g/l and divided by the plate to form two Compartments. Gaps between the plate and the beaker are plugged by fillers. Then the anode is put into one compartment and the cathode is put into another one. A direct current is conducted through the anode and the cathode and a current density is formed on the square hole at 2000A/m^2 while the solution in the beaker is heated to $80\pm 2^\circ\text{C}$. The Luggin's capillary method is used to measure the potential of both surfaces of the membrane square hole. The measured potential difference (V) is regarded as the potential drop across the diaphragm of the laboratory cell. The laboratory cell is conducted with a $100\pm 0.3\text{A}$ direct current and heated to its solution to $80\pm 2^\circ\text{C}$. Then, the cell is operating under same conditions as that of an industrial cell. Within each hour, the difference of levels H was held at $10\pm 0.5\text{cm}$, and the concentration of NaOH of the electrolyte was measured at a time interval of 30 minutes, When the difference of concentration of the solution is less than 10% for four consecutive measurements, the average of last two measurements is regarded as C. From values of D, V, H and C, $K=V/CHD^2$ may be obtained as following:

H(cm)	D(nm)	V(volt)	C(g/l)	$10^6 K=V/CHD^2(\text{v/g})$
10	2500	0.25	18.1	2.08
10	2500	0.40	30.2	2.03
10	2500	0.60	39.8	2.45
10	1500	0.20	29.8	2.96
10	1500	0.40	65.1	2.25
10	1500	0.50	80.2	2.76
10	1000	0.15	69.6	3.00
10	1000	0.30	120.3	3.33
10	1000	0.40	149.5	3.33
10	500	0.15	69.7	8.57
10	500	0.30	120.1	10.00
10	500	0.40	150.3	6.66
10	100	0.10	100.8	3.63
10	100	0.12	124.6	3.84
10	100	0.15	155.3	4.00

From literature data, for 300g/l sodium chloride solution at 80°C , $\rho=1.15\text{g/cm}^3$,

$g=981\text{cm/s}^2$, $q=4.14\times 10^{-4}\text{g/A.s}$, $R_0=1.82\text{ohm.cm}$, $\mu=0.53\times 10^{-2}\text{g/cm.s}$. So $10^6K=2.92$ and it is close to the result of this laboratory experiment. In an industrial cell, its electrode is vertical and the density of solution in the cathode compartment is larger over 5% than that in the anode compartment. For this reason, H should be larger than 10cm to prevent the solution flows from the cathodic compartment to the anodic compartment at the bottom of cell, and D should be below 1000nm for a useful industrial diaphragm. The theory of the kinetics of electrode process reveals that the diameter of bubbles that are formed on the surface of electrode is much larger than 1000nm, therefore gases are divided by the diaphragm.

Current micro-porous membrane technique indicates that artificial fibers are hardly to become a porous layer whose mean diameter of pores is below 1000nm, so artificial fibers diaphragms are not suitable.

Multi-layers of thick micro-porous membrane may become a good performance diaphragm, but they are very expensive and hard to be assembled into current industrial cells. In addition, they can be easily plugged by sediments of calcium and magnesium hydroxide (formed in the pores), and these sediments are difficult to remove.

From equation (2-3), a thin micro-porous membrane may become a good diaphragm if its pores are small enough. But experiments have shown that it has low strength and low current efficiency.

Past studies had discovered that the main reason causing the reduction of current efficiency is the OH^- ions moving into the anodic compartment from the cathode compartment. This movement is due to the diffusion and migration of ions in the solution. Because the movement is happening in the solution, equation (2-3) can't cover it, even though the movement is through the diaphragm anyway.

III. Relationship between diaphragm structure and current efficiency

Prior studies had discovered that the main factor causing the reduction of current efficiency of a cell is OH^- ions moving through the diaphragm of a cell from cathode compartment into anodic compartment. Current efficiency reduction caused by all other factors is below 1%. The movement is due to diffusion and migration of NaOH .

In a solution, solute movement by diffusion is simultaneously occurring with solvent

movement by osmosis but at opposite direction. When the solution flows with a very slow velocity, the solute movement by diffusion is not influenced by velocity immediately and follows Fick's law. Under normal operation conditions, the solution flows through the diaphragm of a cell at a very slow velocity, so the diffusion of NaOH follows Fick's law. During a time t , the amount of NaOH m is diffused through the diaphragm follows

$$m = tD_L F dc/dx \quad (3-1)$$

Here D_L is the diffusion coefficient, F is total area of passages that NaOH passed through, and dc/dx is the concentration gradient of NaOH.

Let dc/dx approximately equal to $\Delta c/\Delta x$. Here Δc is the concentration difference of NaOH in solutions between the two surfaces of the diaphragm. Because the concentration of NaOH in solution at the surface of diaphragm in the cathode compartment nearly equals to that in the solution of cathode compartment C , and because the concentration of NaOH in the solution at another surface of the diaphragm is very small, we may consider $\Delta c = C$. Δx is the mean length of passages of diaphragm and from (1-2) $L = FR/R_0$. Then we get

$$m = tD_L \Delta c / \Delta x = tD_L CR / R_0 \quad (3-1a)$$

During the same time t , the amount of NaOH produced in the cell that may be calculated from Faraday's law is $I \cdot q \cdot t$ when a direct current I has been conducted. If we denote the rate of the reduction of current efficiency caused by the diffusion of NaOH as $-C.E$, then

$$-C.E = m / Iqt = D_L R_0 C / IqR \quad (3-2)$$

The migration of NaOH is OH^- ions toward the anodic compartment of cell from the cathodic compartment when a direct current has been conducted. According to the theory of conductivity of the electrolyte solution, when a direct current is conducted through an electrolyte solution, ions are forced to move by the potential gradient in the solution, the velocity of ions is $v = M dE/dx$, here M is the mobility of ions and dE/dx is the potential gradient along the migration path. If we assume dE/dx approximately equals to $\Delta E/\Delta x$, here ΔE is the potential drop of diaphragm (as V) and Δx is the mean length of passages of the diaphragm (as L). Recall $V = IR$ and $L = FR/R_0$, then

$$V = M R_0 I / F \quad (3-3)$$

When OH^- ions are moving across the diaphragm toward the anode compartment with a velocity V in the solution, at the same time, the solution is moving across the diaphragm with the velocity w . Because both movements are at opposite directions, the OH^- ions arrive to the anode compartment with the velocity $v-w$. Recall $w = Iq/CF$, so

$$v-w = (M R_0 - q/C) I / F \quad (3-4)$$

If $(M R_0 - q/C) \leq 0$, OH^- ions cannot arrive to the anode compartment by the migration and the current efficiency will not be influenced.

Under normal operation conditions, values of C are controlled as a definite number and data of R_0 and q may be found in literature, but M is hardly found. Let $C = 140\text{g/l}$ and $(M R_0 - q/C) = 0$, the value of M at normal operation condition may be calculated and the value is much larger than the value of M for OH^- ions in an infinite dilution solution at 25°C that is the maximal value found in literature.

From the data of many studies and plants' operations, it is known that the current efficiency of cell is decreased by increasing the-concentration of NaOH of the electrolyte of cell under normal operating conditions. When the concentration of NaOH is less than 140g/l , the current efficiency decreases proportionally, and steadily, with the increase of NaOH concentration. This phenomena can be explained by equation (3-2), because D_L , R_0 , q and R are constants and I is controlled steadily. It can also be explained by the fact that $(M R_0 - q/c) > 0$ and no effects of the migration of OH^- ions.

When the concentration of NaOH of the electrolyte of cell is increasing over 140g/l , the current efficiency of cell will decrease with a faster rate. This phenomenon may be attributed to the effects of both the migration and the diffusion. From equation (3-4), migration of OH^- ions can only be controlled by controlling the concentration, so a useful industrial diaphragm has to have a perfect micro-porous layer to make the NaOH concentration of the electrolyte of cell suitable at normal operation condition as described in equation (2-3).

Usually the concentration of NaOH of the electrolyte of cell is controlled below 140g/l , so the effect of OH^- ions' migration may not be noticed and equation (3-2) is thought as the unique equation and determines the relationship between the current

efficiency of cell and the structure of the diaphragm.

From (3-2), under normal operating conditions, D_L , R_0 and q are nearly constants, and I and C are controlled strictly by operators, so the current efficiency of the cell will increase if R of the diaphragm increases. From (1-2), the value of R is independent of the size of the pores of diaphragm. R of the diaphragm may be increased by adding a thick permeable layer, be it a permeable film, plate or cloth. The thick permeable layer may be made from cheaper materials and with simple processes because pores in it are large enough, while from equation (2-2), Δp is very small when the solution passes through this layer.

The thick permeable layer may be covered on a thin micro-porous membrane layer to form a diaphragm and meet all the requirements for a useful industrial diaphragm. This diaphragm comprises different layers, so it is called as a different layers structure and said above diaphragm is called as a whole porous structure. The current efficiency of these diaphragm may be measured as following.

Using a laboratory cell said above, it is assembled with different kind of diaphragms in each test. Before the diaphragm is assembled, D and V are measured with the process said above. The laboratory cell is operated under conditions said above except to have a controlled level difference of H to control the concentration of NaOH of electrolyte C to $120 \pm 5 \text{ g/l}$. When C is $120 \pm 5 \text{ g/l}$, holding C steadily. At a half hour interval and for two hours, the electrolyte of cell is collected in a vessel. Then the volume and the concentration of NaOH of the electrolyte may be measured strictly to get amounts of NaOH produced during this time. The amount of NaOH generation is also obtained from theoretical calculation from the current intensity (I) and the operation time (t), therefore the current efficiency of cell may be calculated. The data are shown as below:

Kind of diaphragm	$D(\text{nm})$	$V(\text{volt})$	$C(\text{g/l})$	Current efficiency(%)
Whole porous structure	500	0.12	120 ± 5	91.2
Whole porous structure	500	0.15	120 ± 5	92.3
Whole porous structure	500	0.22	120 ± 5	94.1
Different layers structure	500	0.13	120 ± 5	91.1
Different layers structure	500	0.21	120 ± 5	93.6
Different layers structure	250	0.11	120 ± 5	91.5
Different layers structure	250	0.16	120 ± 5	93.5

It can be seen from the data that the diaphragm of different layers' structure may become a useful industrial diaphragm. From (3-2), $-C.E$ decreases with the increase of I . If the cell is operated under a higher current density, a higher current efficiency may be achieved. Because the different layers' structure diaphragm has a much higher strength than the asbestos diaphragm does, the cell employing different layers' diaphragm may be operated at a current density up to $3000A/m^2$ or higher, thus the cell can have a higher current efficiency.

IV. Conclusion

In history, cement, stoneware and asbestos cloth adding barium sulphate were used as diaphragms, but few studies were conducted on these materials although they were of stable or semi-stable structure. A lot of studies on past diaphragms were focused on the deposition asbestos diaphragm assuming it had a stable structure in the operation circle, but this is a wrong assumption. Past studies on non-asbestos diaphragms followed the same wrong assumption as they assumed for the deposition asbestos diaphragm. A lot of them believed that some artificial fibers may function as an industrial diaphragm as asbestos fibers do and all of them believed that whole micro-porous structure of the deposition asbestos diaphragm was the unique reasonable structure. That's why they failed to find a useful industrial diaphragm and it is imperative to redefine a new theory for the structure of diaphragm in order to provide guidance on the study of non-asbestos diaphragms.

It is concluded that a useful industrial diaphragm has to have both a perfect micro-porous layer whose mean diameter of pores is below 1000 nm and a suitable resistance in the operation circle. The deposition asbestos diaphragm has an unstable structure, so it is hard to sustain a longer operation circle and the direct current changes drastically. Non-asbestos diaphragms should have a stable structure and a perfect micro-porous layer whose mean diameter of pores is below 1000 nm. If they mimic the deposition asbestos diaphragm, they will hardly become the useful industrial diaphragm because the perfect micro-porous layer may only be obtained with the membrane technique and because the micro-porous membrane is expensive, especially when it is made from a material that should tolerate the cell operating condition. Membranes whose strength and resistance are sufficient are normally thick, very expensive, blocked easily and difficult to be assembled into current cells.

From this study, another conclusion is that the perfect micro-porous layer and the

suitable resistance may be got from different layers in a diaphragm. Therefore, a thin micro-porous membrane (made from fluoride containing polymers) and some permeable films (made from cheaper materials) that are covered with each other may form a non-asbestos diaphragm. This diaphragm, that is treated by special processes and become more applicable to a cell, has excellent performances and a reasonable price. It has been named as permeable membrane diaphragm of different layers for electrolytic cell or different layers diaphragm.

The different layers diaphragm has been used in aforementioned tests in a laboratory cell. Usually the operation condition of cell was around the direct current 10A, concentrate of NaOH 120g/l, current efficiency 95% and the cell volts 3.2v, sometimes the current reduced to nearly zero and raised to 15A rapidly repeated over twenty times in a test circle. Some tests lasted over eleven months. All diaphragms achieved normal performances through the end of the test period.

A patent application for the different layers diaphragm have been published as WO 00/46425.